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CONTRIBUTIONS FROM THE CHEMICAL LABORATORY OF
HARVARD COLLEGE.

THE STANDARD OF ATOMIC WEIGHTS.

BY THEODORE WILLIAM RICHARDS.

Received July 27, 1901.

The long continued discussion concerning the relative advantages of hydrogen and oxygen as standards of the numerical values of chemical combining weights seems to need yet another word. In spite of the fact that an international committee has decided by a large majority in favor of oxygen, the opposing arguments have not been put to rest.

The latest paper on this subject is by Erdmann,* the well known champion of the old unit value for hydrogen and the new value for every other atomic weight. The paper consists mainly of a partial reply to an earlier paper by Brauner.† The weight of the argument in these papers seems to be distinctly on Brauner's side, but it is not my purpose to recapitulate all the arguments which these gentlemen and others have advanced.‡ I wish rather to call attention to a few points which do not seem to have received the attention which they deserve.

The first of these concerns the question of fact. What element has served as the actual standard of comparison in a plurality of cases? The question is easily answered by referring to Clarke's valuable compilation.§

Evidently hydrogen in combination has been weighed accurately only in the cases of water and the ammonium salts. The atomic weights of zinc, aluminum, iron, nickel, cobalt, and gold have been determined by

* Zeitschrift für anorg. Chem., 27, 127 (1901).

† Zeitschrift für anorg. Chem., 26, 186 (1901).

‡ A recent recapitulation of many of the arguments on each side may be found in the report of the American Chemical Society's branch of the International Committee, published in the Journal of the American Chemical Society, February, 1901, p. 44 of the Proceedings.

§ F. W. Clarke, A Recalc. of the At. Weights, Smithsonian. Misc. Coll., The Constants of Nature, Part V. (1897).

measuring or weighing the hydrogen which they displace or to which they correspond, but the results of different experimenters are far from concordant. All other elements beside these eight have been referred to hydrogen only with the assistance of oxygen.

On the other hand, oxygen has been used as the direct standard of reference in countless cases. The determination of oxygen in the chlorates, bromates, and iodates may be considered as the starting-point for the calculation of Ag, K, Na, Cl, Br, and I, and through them of very many others. Into this remarkable series of experiments, executed in great measure by Stas, the value of hydrogen enters only in the case of ammoniac salts. If the atomic weight of nitrogen were certain, we should indeed have here a direct basis of comparison, but unfortunately the value for this element may be as much as 0.05 per cent, or even more, in error. The direct practical determination of the exact composition of ammonia gas, either by analysis or synthesis, has not yet been accomplished. The value for nitrogen depends largely upon the analysis or synthesis of nitrates, thus making oxygen the essential standard of reference in this case also. The other elements which have been determined more or less accurately by reference to oxygen are as follows: H, C, Cu, Ca (through the carbonate), Pb (through the nitrate), Zn, Cd, Hg, Tl (through the nitrate), Sn, P, As, Sb, Bi, Mo, U, W, Se, Te, Mn, Fe, Ni, Co. If one adds to these all those which are connected less directly with oxygen through the halogen and silver values and the sulphates, all the chemical elements are included in the list. Thus an overwhelming majority of elements is referred more directly to oxygen than to hydrogen.

Erdmann points out in his recent paper that there are possible causes of error in some of the methods used by Stas for the analysis of chlorates. Unfortunately he does not touch upon the very important question of the percentage effect of these causes of error. It is undoubtedly true that in these cases, as well as in every other case, absolute accuracy was not attained. No analytical method is wholly free from the possibility of error, and hence it is vain to expect that any table of atomic weights should be perfectly trustworthy. When the accuracy of Stas has been exceeded in actual fact, it will be time to forsake his results for the newer values.

Erdmann suggests that silver be chosen as the standard of reference, and the suggestion is one which has some advantages. On the other hand the tendency which this metal has to absorb oxygen has cast a suspicion over some of the work in which it was used. A further objection

to silver lies in the fact that it cannot be directly used in the demonstration of Avogadro's rule. Moreover, one is in doubt as to the value to assign to this element, supposing that it should be selected as the standard. According to Erdmann's earlier arguments, logically followed out, one should make silver 100.000, but this would cause hydrogen to be less than unity. If silver is taken as 107.11, hydrogen would be 1.000 at the present time, but what it might be in the future no one can predict, since hydrogen is compared with silver at present only in a roundabout fashion. Hence each of these assumptions would bring with it a further disadvantage besides that attending the immediate inconvenience of using new values.

The most important argument used by the minority is the pedagogic one. It is contended that the uneven value for hydrogen, 1.0075, complicates the explanation of the very important rule of Avogadro. If this were true, it would indeed be worthy of consideration, but according to my experience there is no difficulty in the matter.

For some time I have abandoned the comparison of specific gravities as a means of demonstrating Avogadro's rule. I have used instead the *densities* of gases and vapors, — that is, the actual weights of a litre of the several substances at 0°C, or at 273°C or at 546°C. This seems to be a more successful method, probably because density has concrete dimensions, and is not a numerical abstraction as specific gravity is.

The student at once comprehends the equation of ratios $\frac{1.97}{1.43} = \frac{x}{32}$.

If the exact experimental values for the densities of the two gases are given, the solution of this equation gives the student not only the observed molecular weight of carbon dioxide, but also an insight into the extent of the actual deviations from Avogadro's rule. Since the introduction of this method of presentation, I have had far less trouble, and far more successful examination results, than were formerly obtained. The student usually learned by heart the old rule, "The molecular weight equals twice the specific gravity," without understanding it. Because the density-method would serve equally well with any gas used as a standard, the pedagogic argument against $H = 1.0075$ seems to me illusory.

The argument just discussed has led the Committee of the German Chemical Society to an action which seems to me exceedingly unfortunate, — namely, the publication of *two* tables of atomic weights. This action has already been criticised by Küster and others. Either table alone, supported by suitable weight of opinion, would have been vastly

better than two. The mistake is especially to be regretted because the eminent committee in question has previously acted with so much wisdom and ability.

It seems to me that by far the most important questions which have been raised in the whole discussion are the questions of uniformity and permanence of usage. These were indeed the prime objects of the foundation of the German Committee in the first place. Nothing could be more destructive to accurate calculation than a changeable standard of measurement; and yet this very uncertainty marks the present state of affairs.

I cannot but think that every one should accept the standard of reference upon which any considerable majority of representative chemists agree, since the matter is rather a question of convenience than a question of principle. In the first place I preferred $O = 16.000$ primarily because so much valuable work, both in analytical and in physical chemistry, has already been calculated upon this basis, and because of the effect of a possible change in the oxygen-hydrogen ratio. At present a still more important reason for preferring this standard exists, namely the action of the International Committee, consisting of some of the most prominent chemists of many countries, appointed for the express purpose of voting upon this question. This Committee, by a large majority, decided to call oxygen exactly 16.000. I cannot avoid the belief that until a yet more representative body of chemists is appointed by international co-operation, or until the present committee reconsiders its vote in parliamentary fashion, the present verdict of this committee should rule the chemical world. Unless chemists are prepared to accept such a ruling, the appointment of an international committee is a waste of time.

Representative government in civil affairs would be impossible if the minority refused to act in accordance with the decision of the majority. Does not the same principle apply to scientific rulings? Of course intelligent *discussion* is always desirable—the restriction applies to action and not to speech. Before the action of the International Committee the situation might have been called one of scientific barbarism, but at present it may be called one of scientific rebellion.

Formerly new determinations of atomic weights made at Harvard were expressed in publication both upon the basis $O = 16.000$ and upon the basis $O = 15.879$, because the question had not been decided by representative vote. In future, out of respect to the action of the International Committee, only the former standard will be used in this

Laboratory. If an adequate internationally representative body of chemists should in the future decide that some other standard is better, immediate change of practice will be made to suit the new decision. One regrets that so much time should have been spent in discussing a matter which involves no fundamental principle, but is simply a question of form and of convenience.

The subject matter of the present paper may be summed up in the following sentences. It is pointed out that oxygen has actually served as the experimental standard of reference in a great majority of cases, that a great bulk of valuable work has already been published on the basis $O \doteq 16.000$, and that the use of this standard involves no important didactic difficulties. It is further contended that the decision of the representative International Committee is in itself an important reason for adopting this standard, and that uniformity of usage is more important than any of the special advantages claimed by either side in the discussion.

SEAL HARBOR, MT. DESERT, MAINE,
July 22, 1901.